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# THE TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM IN MIXED CHLORIDE SOLUTION

BY

J. LOWE HALL

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

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COLLEGE OF LIBERAL ARTS AND SCIENCES

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June 9, 1919

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Joseph Lowe Hall

ENTITLED Transference Numbers of Sodium and Potassium in Mixed Chloride Solution.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering

S. A. Braley
Instructor in Charge

APPROVED: W. A. Noyes

HEAD OF DEPARTMENT OF Chemistry.

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# TRANSFERENCE NUMBERS OF SODIUM AND POTASSIUM IN MIXED CHLORIDE SOLUTION

## A. Introduction

### 1. The Purpose of the Investigation.

T. R. Ball (1) has found in a study of equilibria between mixed salt solutions and liquid amalgams, that in the case of equivalent mixtures of NaCl and KCl in aqueous solution, the simple ion fraction of potassium falls off with increase of total salt concentration. The same conclusion has been reached in other work of similar nature which has been carried on in this laboratory under Dr. G. Mc P. Smith. Ball suggests the possibility of the formation of complex ions in explaining his results, and further suggests that "transference experiments would probably throw additional light upon this subject".

Consequently this investigation was undertaken with the purpose of obtaining relations between transference numbers of Na and K in equivalent mixtures of their chlorides, the effect of varying the concentration, and a comparison with results calculated on the basis of the isohydric principle and the principles of conductance.

### 2. Some Principles Relating to Transference and Ionization of Salts in Mixtures.

According to the theories of transference (2) the passage of a current through a solution of an electrolyte is effected by the migration of the positive and negative ions under the influence of the P. D. set up between the electrodes, and their subsequent carrying and releasing of ionic charges upon the respective electrodes of opposite electric character. In this manner anions continually

migrate into the anode portion, and cations into the cathode portion.

G. M. J. McKay (3) by the use of transference experiments on mixed solutions of KCl and $K_2SO_4$, 0.2009 N with respect to each, has shown that the ratio of the ionization factors of the two salts in the mixture is 1.372, whereas the ratio as calculated from the conductance of the solution and the isohydric principle is 1.275. And in general, principles based on conductivity do not yield values in agreement with those obtained by other methods.

In this investigation, in which two kinds of cations are present, the respective amounts of those two ions migrating to the cathode will depend upon their respective concentrations and mobilities. And if each salt ionizes in the mixture just as it would in its simple solution at that same total concentration of common ion ($Cl^-$), - according to the isohydric principle (2),- then the ratio of the ion migrations should correspond to values calculated on the basis of that principle,- assuming that the ratio of the ion mobilities in the mixture is the same as their ratio in simple solutions at same total salt concentration.

On the other hand any complex ion which might form containing quantities of both Na and K in the same aggregate, and possessing an individual mobility and ionic character, would cause an abnormal transference of those two elements, in the light of the above considerations. Many examples of double salts are known in which the alkali halides appear, such as $K_2PtCl_6$, $KCl \cdot MgCl_2 6H_2O$, $Na_3AlF_6$, $2NaCl \cdot Al_2Cl_6$, the KI complexes with the iodides of Cd, Hg, Zn, and Bi, etc. Also unstable complexes are known to exist in solution, such as $KI_3$. It is therefore not altogether rash to expect that the alkali halides form complexes with each other in solution, especially as their ions are

known to be hydrated (4).

## B. Theoretical

If the KCl and NaCl ionize in their mixed solutions as they do in simple solutions, three kinds of ions will be engaged in carrying the electricity in a transference experiment, and the sum of the amounts each carries must equal the total amount of electricity passed through the solution. That is,-

$$N_e = N_K + N_{Na} + N_{Cl} \qquad (1)$$

where $N_e$ represents the total number of equivalents of electricity passed, and the others the respective amounts carried by each kind of ion. The transference number of an ion is the fraction of the total amount of electricity passed which is carried by that ion, that is,-

$$T_{Na} = \frac{N_{Na}}{N_e}, \text{ and } T_K = \frac{N_K}{N_e}, \text{ etc.} \qquad (2)$$

From this we may directly obtain the ratio,-

$$\frac{T_{Na}}{T_K} = \frac{N_{Na}}{N_K} \qquad (3)$$

Furthermore the amount of electricity carried by each kind of ion is proportional to the concentration of that ion and its mobility, and the latter is in turn proportional to the equivalent conductance of the ion (2). That is,-

$$N_{Na} = k\, C_{Na+} \cdot U_{Na+} = k'\, C_{Na+} \cdot \Lambda_{Na+} \qquad (4)$$

Substituting this expression and a similar one for $N_K$ in equation (3), and expressing the ion concentration by the product of the salt concentration into the ionization factor, we obtain, the ratio,-

$$\frac{T_{Na}}{T_K} = \frac{C_{NaCl} \cdot \alpha_{NaCl} \cdot \Lambda_{Na^+}}{C_{KCl} \cdot \alpha_{KCl} \cdot \Lambda_{K^+}} \qquad (5)$$

In the above equation the left hand part may be obtained directly from the experimental data, and the right hand part may be solved by the use of conductance data from simple solutions corresponding to the total salt concentration of the mixture in accordance with the isohydric principle. If we assume $\alpha = \Lambda/\Lambda_o$, and as the concentrations of the two salts in the mixture were the same in each case, equation (5) may be expressed for the purposes of this work,-

$$\frac{T_{Na}}{T_K} = \frac{\Lambda_{NaCl} / \Lambda_{o\,NaCl} \cdot \Lambda_{Na^+}}{\Lambda_{KCl} / \Lambda_{o\,KCl} \cdot \Lambda_{K^+}} \qquad (6)$$

Since equivalent ion conductances are known only at infinite dilution, it is necessary to assume, as McKay does (3), that the ratio of these values for sodium and potassium ions is the same as at infinite dilution. Also as Washburn (2) and McKay (3) both observe that in the case of two strong electrolytes in a mixed solution, ionization calculations based on total salt concentration agree quite closely with those based on the common ion concentration, the former will be used in calculations. As viscosity corrections would be applied alike to numerator and denominator, they will be omitted.

## C. Materials, Apparatus and Method of Experimentation.

1. Materials.- (a) Sodium and Potassium Chlorides.

A supply of these salts were on hand, having been prepared by others during the previous year for the same purpose. They were prepared by precipitating a good commercial grade of the salts in aqueous solution with HCl gas two times, centrifuging and drying in

an electric muffle at about 750° C. They were stored in glass stoppered bottles, and again dried in the muffle in quantities as used.

(b) Coulometer Materials.- 15 grams of crystalline C. P. Ag $NO_3$ were dissolved in 150 c.c. of distilled water shortly before using. This amount of solution just conveniently filled both coulometers.

A pure grade of silver (99.9% fine) was very kindly supplied by Dr. D. F. McFarland for anodes. The silver was melted on a bone ash cupel by means of a blast lamp. A piece of heavy silver wire was inserted into the molten silver button, and the mass allowed to solidify.

A weighed Pt dish was used as a cathode.

(c) Silver Chloride for Cathode.- The $AgNO_3$ solution from the coulometers used in the previous run was kept in a dark place to be used in preparation of Ag Cl for the succeeding run. It was filtered, heated to boiling, and precipitated with a hot solution of a little more than theoretical amount of NaCl. The adherent, pasty precipitate was finely disintegrated with a glass spatula, washed by decantation two or three times, and finally transferred to a filter and thoroughly washed. The precipitate was then washed with some of the stock solution of mixed chlorides and transferred to the apparatus. According to Washburn (5), "It has been found that the physical condition of the Ag Cl plays an important part ---. If it is prepared by precipitating in the cold, it fails to act as a depolarizer."

(d)The Anode.- The anode was prepared essentially as the "Type B Anode" described by Washburn (5) for use in transference experiments. A coil of silver wire was wound to fit inside of a small size Soxhlet extraction cartridge. The remaining space was packed with crystals of electrolytic silver obtained from the coulometer deposits, and the

cup pierced in several places with a needle.

2. Apparatus and Method of Experimentation.-

(a) Apparatus.- The same apparatus was used as E. W. Washburn has used and fully described (5) for the measurement of transference numbers. The special coulometer stands were equipped with a glass rod support.

(b) Method of Manipulation.- Essentially the same procedure was followed as described by Washburn (5). The solution of salts was prepared by weighing out the theoretical amounts of the two dried salts, dissolving in distilled water, and transferring quantitatively to a tared, standardized, volumetric flask. After being made up to volume the entire was weighed to the nearest milligram, from which the "equivalents per 100 g. of water" was obtained.

An impressed E. M. F. of 20 volts was used, and a current of 20-40 milliamperes. A coulometer was included in the circuit at both ends of the apparatus.

The three middle portions were weighed in a tared, standardized 100 c.c. volumetric flask (250 c.c. at the highest concentration used), made up to volume and transferred to a clean, dry, glass-stoppered Earlenmeyer flask. The end portions were weighed to the nearest milligram in the apparatus, and later transferred to the volumetric flask and made up to volume. This was done in order to facilitate the matter of taking samples for analysis, as 10 c.c. portions could be taken with a standardized pipette.

(c) Pipette, Burettes, and Weights.- A. U. S. Bureau of Standards 10 c.c. pipette was used for taking samples; it was cleaned with cleaning solution, thoroughly rinsed with distilled water, and subsequently with small portions of the solution for analysis.

The burettes were also standardized and had a capacity of 30 c.c., reading approximately to 0.01 c.c. in accuracy.

The weights were calibrated against a set of standard weights, and the proper corrections were applied to all weights of salts for the solutions and to all analytical weighings.

(d) Thermostat.- A large Freas thermostat electrically controlled was filled with water to a depth sufficient to cover the horizontal section of the apparatus. The temperature was accurate to less than a tenth of a degree and constant to less than one hundredth of a degree.

3. Analysis and Calculations.-

(a) Analysis.- Duplicate samples from the end portions and one from each of the three middle portions were transferred to small porcelain evaporating dishes for a sodium - potassium determination. At the same time an entire duplicate set of samples was transferred to Jena glass beakers (600 c.c. capacity) for a Volhard volumetric determination of chlorine.

For the Volhard titration the samples were diluted with 100 c.c. distilled water, six or seven drops of conc. $HNO_3$ added, the Cl precipitated with an excess of N/10 $AgNO_3$ (standardized against pure NaCl), filtered, and the filtrate titrated with N/20 KCNS, with ferric alum as an indicator. This analysis was used merely as a check on the total equivalents of salt as found by the chlorplatinate method.

The sodium - potassium determination was carried out by the chlorplatinate method as described by Ball (1), with the exception that methyl alcohol (redistilled on a steam bath) was used instead of ethyl alcohol as a separating medium. Care was taken to allow the

last traces of the methyl alcohol to evaporate, however, before washing down the filter with hot water and evaporating on the steam bath, as the alcohol exerts a strong reducing effect on the platinum salts when heated. The chlorplatinic acid was also prepared as described by Ball.

(b) Calculations.- The factor 0.3056 was applied to the weight of the $K_2PtCl_6$ to obtain the weight of KCl; the Na Cl was determined by difference from the weight of the mixed chlorides. The weight of water in the portion was found by subtracting the weight of the mixed chlorides from the weight of the portion. Knowing the number of equivalents of each salt originally dissolved in that weight of water, we can determine how much of each salt has been transferred from the anode and to the cathode. The number of equivalents of each cation transferred divided by the average deposit of silver (in equivalents) in the two coulometers give the transference numbers of those ions. The atomic weights used are, Na = 23.0; K = 39.1; Cl = 35.46; and Ag = 107.88.

## D. Experimental Data

The following tables contain the experimental data obtained in this investigation, and are for the most part self explanatory. the number of equivalents of each salt found by the chlorplatinate analysis were added, and the sum compared with the result obtained by the Volhard titration as means of a check. The basis for comparison with calculated, or theoretical data is in the ratio, $T_{Na}/T_K$, as shown in equation (6) in the theoretical part. Conductance data of reliable character covering the range of concentration, and at the temperature used were difficult to find. However, values for $\Lambda$ determined by

TABLE I

Temp. 25° C. Total Normality 0.2

Equivalent mixture of NaCl and KCl 0.01008 equiv's. of each salt per 100 g. water

| Portions | Anode (a) | Anode (b) | Anode Middle | Middle | Cathode Middle | Cathode (a) | Cathode (b) |
|---|---|---|---|---|---|---|---|
| Sample (from 100 c.c. total) | 20.0c.c. | 20.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Wt. mixed chlorides, grams | 0.1053 | 0.1050 | 0.1341 | 0.0667 | 0.1336 | 0.1619 | 0.1627 |
| Wt. of $K_2PtCl_6$ | 0.1570 | 0.1564 | 0.2403 | 0.1243 | 0.2465 | 0.3187 | 0.3192 |
| Wt. of KCl from $K_2PtCl_6$ | 0.0479 | 0.0478 | 0.0734 | 0.0380 | 0.0753 | 0.0973 | 0.0975 |
| Wt. of NaCl (by difference) | 0.0574 | 0.0572 | 0.0607 | 0.0287 | 0.0583 | 0.0646 | 0.0652 |
| Equiv's. of KCl in portion | .003211 | .003205 | .00985 | .00510 | .01010 | .01305 | .01307 |
| Equiv's. of NaCl in portion | .004910 | .004894 | .01038 | .00491 | .00998 | .01105 | .01115 |
| Total equiv's. of Cl in portion | .008121 | .008099 | .02023 | .01001 | .02008 | .02410 | .02422 |
| Same by Volhard titration | .008085 | .00800 | .02006 | .00997 | .01994 | .02415 | .02415 |
| Wt. of portions, grams | 83.511 | ——— | 100.503 | 59.944 | 100.493 | ——— | 78.593 |
| Wt. of water in portions | 82.985 | ——— | 99.162 | 59.277 | 99.157 | ——— | 76.970 |
| Equiv's. of each salt originally in portion | .008365 | ——— | .0100 | .00598 | .0100 | ——— | .00776 |
| Equiv's. of K transferred | .005154 | .005160 | ——— | ——— | ——— | .00529 | .00531 |
| Equiv's. of Na transferred | .003455 | .003471 | ——— | ——— | ——— | .00329 | .00339 |
| Wt. of Ag in coulometer | 2.1582 | ——— | ——— | ——— | ——— | ——— | 2.1576 |
| Equiv's. of elec. passed (ave.) | 0.0200 | ——— | ——— | ——— | ——— | ——— | ——— |
| Transference number of K | 0.2577 | 0.2580 | ——— | ——— | ——— | 0.2645 | 0.2655 |
| Transference number of Na | 0.1727 | 0.1735 | ——— | ——— | ——— | 0.1645 | 0.1695 |
| Ratio $T_{Na}/T_K$ | 0.670 | 0.672 | ——— | ——— | ——— | 0.608 | 0.638 |

TABLE II

Temp. 25° C. Total Normality 0.2

Equivalent mixture of NaCl and KCl 0.01008 equiv's. of each salt per 100 g. water

| Portions | Anode (a) | Anode (b) | Anode Middle | Middle | Cathode Middle | Cathode (a) | Cathode (b) |
|---|---|---|---|---|---|---|---|
| Sample (from 100 c.c. total) | 20.0c.c. | 20.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Wt. of mixed chlorides, grams | 0.0743 | 0.0744 | 0.1228 | 0.0781 | 0.1279 | 0.1714 | 0.1714 |
| Wt. of $K_2PtCl_6$ | 0.0983 | 0.0987 | 0.2268 | 0.1445 | 0.2354 | 0.3372 | 0.3336 |
| Wt. of KCl from $K_2PtCl_6$ | 0.0300 | 0.0301 | 0.0693 | 0.0441 | 0.0719 | 0.1030 | 0.1019 |
| Wt. of NaCl (by difference) | 0.0443 | 0.0443 | 0.0535 | 0.0340 | 0.0560 | 0.0684 | 0.0695 |
| Equiv's. of KCl in portion | .002014 | .02022 | .009296 | .005922 | .009671 | .013820 | .013670 |
| Equiv's. of NaCl in portion | .003789 | .003780 | .00915 | .00582 | .00958 | .01170 | .01189 |
| Total No. of equiv's. in portion | .005803 | .005802 | .018446 | .011742 | .019251 | .02552 | .02556 |
| Same by Volhard titration | .00677 | .00675 | .01893 | ——— | .01936 | .02551 | .02551 |
| Wt. of portions, grams | 74.300 | ——— | 94.720 | 59.237 | 97.386 | ——— | 78.774 |
| Wt. of water in portions | 73.928 | ——— | 93.492 | 58.456 | 96.107 | ——— | 77.060 |
| Equiv's. of each salt originally in portion | .007452 | ——— | .00942 | .00589 | .00968 | ——— | .00777 |
| Equiv's. of K transferred | .005438 | .005430 | ——— | ——— | ——— | .00605 | .00590 |
| Equiv's. of Na transferred | .003663 | .003672 | ——— | ——— | ——— | .00393 | .00412 |
| Wt. of Ag in coulometer | 2.5702 | ——— | ——— | ——— | ——— | ——— | 2.5704 |
| Equiv's. of electricity passed (ave.) | .023825 | ——— | ——— | ——— | ——— | ——— | ——— |
| Transference number of K | 0.2282 | 0.2279 | ——— | ——— | ——— | 0.2540 | 0.2477 |
| Transference number of Na | 0.1538 | 0.1541 | ——— | ——— | ——— | 0.1649 | 0.1729 |
| Ratio $T_{Na}/T_K$ | 0.6738 | 0.6762 | ——— | ——— | ——— | 0.6495 | 0.6982 |

TABLE III

Temp. 25° C. Total Normality 0.4

Equivalent mixture of NaCl and KCl 0.02025 equiv's. of each salt per 100 g. water

| Portions | Anode (a) | Anode (b) | Anode Middle | Middle | Cathode Middle | Cathode (a) | Cathode (b) |
|---|---|---|---|---|---|---|---|
| Sample (from 100 c.c. total) | 10.0c.c. | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Wt. mixed chlorides, grams | 0.1409 | 0.1410 | 0.2506 | 0.1463 | 0.2638 | 0.2754 | 0.2749 |
| Wt. of $K_2PtCl_6$ | 0.2340 | 0.2351 | 0.4568 | 0.2678 | 0.4840 | 0.5291 | 0.5286 |
| Wt. of KCl from $K_2PtCl_6$ | 0.0715 | 0.0718 | 0.1397 | 0.0818 | 0.1480 | 0.1617 | 0.1615 |
| Wt. of NaCl (by difference) | 0.0694 | 0.0692 | 0.1104 | 0.0645 | 0.1158 | 0.1137 | 0.1134 |
| Equiv's. of KCl in portion | .00959 | .00963 | .01872 | .01097 | .01988 | .02166 | .02164 |
| Equiv's. of NaCl in portion | .01187 | .01184 | .01898 | .01103 | .01981 | .01945 | .01940 |
| Total equiv's. of Cl in portion | .02146 | .02147 | .03770 | .02200 | .03969 | .04111 | .04104 |
| Same by Volhard titration | .02141 | .02137 | .03763 | .02191 | .03955 | .04095 | .04095 |
| Wt. of portions, grams | 82.333 | ——— | 95.625 | 55.715 | 101.401 | ——— | 81.991 |
| Wt. of water in portions | 80.924 | ——— | 93.119 | 54.252 | 98.763 | ——— | 79.239 |
| Equiv's. of each salt originally in portion | .016387 | ——— | .01886 | .01098 | .0200 | ——— | .016046 |
| Equiv's. of K transferred | .00680 | .00676 | ——— | ——— | ——— | .00561 | .00559 |
| Equiv's. of Na transferred | .00452 | .00455 | ——— | ——— | ——— | .00340 | .00335 |
| Wt. of Ag in coulometer | 2.7724 | ——— | ——— | ——— | ——— | ——— | 2.7650 |
| Equiv's. of elec. passed (ave.) | .02566 | ——— | ——— | ——— | ——— | ——— | ——— |
| Transference number of K | 0.2651 | 0.2634 | ——— | ——— | ——— | 0.2187 | 0.2179 |
| Transference number of Na | 0.1762 | 0.1773 | ——— | ——— | ——— | 0.1325 | 0.1305 |
| Ratio $T_{Na}/T_K$ | 0.665 | 0.673 | ——— | ——— | ——— | 0.606 | 0.599 |

TABLE IV

Temp. 25° C. Total Normality 0.4

Equivalent mixture of NaCl and KCl 0.02025 equiv's. of each salt per 100 g. water

| Portions | Anode (a) | Anode (b) | Anode Middle | Middle | Cathode Middle | Cathode (a) | Cathode (b) |
|---|---|---|---|---|---|---|---|
| Sample (from 100 c.c. total) | 10.0cc. | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Wt. mixed chlorides, grams | 0.1568 | 0.1570 | 0.2530 | 0.1451 | 0.2650 | 0.2624 | 0.2623 |
| Wt. of $K_2PtCl_6$ | 0.2645 | 0.2653 | 0.4607 | 0.2670 | 0.4860 | 0.5018 | 0.5001 |
| Wt. of KCl from $K_2PtCl_6$ | 0.0808 | 0.0811 | 0.1407 | 0.0816 | 0.1484 | 0.1642 | 0.1637 |
| Wt. of NaCl (by difference) | 0.0760 | 0.0759 | 0.1123 | 0.0635 | 0.1166 | 0.0982 | 0.0986 |
| Equiv's. of KCl in portion | .01084 | .01087 | .01890 | .01095 | .01992 | .02202 | .02195 |
| Equiv's. of NaCl in portion | .01300 | .01298 | .01920 | .01086 | .01993 | .01680 | .01686 |
| Total equiv's. of Cl in portion | .02384 | .02385 | .03810 | .02181 | .03985 | .03882 | .03881 |
| Same by Volhard titration | .02383 | .02383 | .03817 | .02184 | .03982 | .03928 | .03922 |
| Wt. of portions, grams | 85.012 | ——— | 96.407 | 55.255 | 101.559 | ——— | 79.363 |
| Wt. of water in portions | 83.443 | ——— | 93.877 | 53.774 | 98.909 | ——— | 76.740 |
| Equiv's. of each salt originally in portion | .016901 | ——— | .01901 | .01089 | .02002 | ——— | .01554 |
| Equiv's. of K transferred | .006061 | .006030 | ——— | ——— | ——— | .00648 | .00641 |
| Equiv's. of Na transferred | .003901 | .003921 | ——— | ——— | ——— | .00126 | .00132 |
| Wt. of Ag in coulometer | 2.3853 | ——— | ——— | ——— | ——— | ——— | 2.3850 |
| Equiv's. of elec. passed (ave.) | .02211 | ——— | ——— | ——— | ——— | ——— | ——— |
| Transference number of K | 0.2741 | 0.2728 | ——— | ——— | ——— | 0.2931 | 0.2899 |
| Transference number of Na | 0.1764 | 0.1773 | ——— | ——— | ——— | 0.057 | 0.059 |
| Ratio $T_{Na}/T_K$ | 0.636 | 0.650 | ——— | ——— | ——— | 0.195 | 0.204 |

TABLE V

Temp. 25° C. Total Normality 1.6

Equivalent mixture of NaCl and KCl 0.083552 equiv's. of each salt per 100 g. water

| Portions | Anode (a) | Anode (b) | Anode Middle | Middle | Cathode Middle | Cathode (a) | Cathode (b) |
|---|---|---|---|---|---|---|---|
| Sample (from 100 c.c. total) | 10.0c.c. | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 | 10.0 |
| Wt. mixed chlorides, grams | 0.3004 | 0.3008 | 0.3999 | 0.2512 | 0.4008 | 0.3601 | 0.3603 |
| Wt. of $K_2PtCl_6$ | 0.5385 | 0.5387 | 0.7344 | 0.4604 | 0.7357 | 0.6727 | 0.4731 |
| Wt. of KCl from $K_2PtCl_6$ | 0.1645 | 0.1646 | 0.2244 | 0.1377 | 0.2248 | 0.2056 | 0.2057 |
| Wt. of NaCl (by difference) | 0.1359 | 0.1362 | 0.1755 | 0.1135 | 0.1760 | 0.1545 | 0.1546 |
| Equiv's. of KCl in portion | 0.05518 | 0.05520 | 0.07525 | 0.04620 | 0.07540 | 0.06892 | 0.06895 |
| Equiv's. of NaCl in portion | 0.05812 | 0.05825 | 0.07510 | 0.04855 | 0.07520 | 0.06607 | 0.06610 |
| Total equiv's. of Cl in portion | 0.11330 | 0.11345 | 0.15035 | 0.09475 | 0.15060 | 0.13499 | 0.13505 |
| Same by Volhard titration | 0.1136 | 0.1135 | 0.1506 | 0.09438 | 0.1508 | 0.1352 | 0.1352 |
| Wt. of portions, grams | 83.902 | ——— | 100.190 | 62.990 | 101.481 | ——— | 83.845 |
| Wt. of water in portions | 76.287 | ——— | 90.193 | 56.710 | 91.461 | ——— | 74.840 |
| Equiv's. of each salt originally in portion | 0.06359 | ——— | 0.07536 | 0.04738 | 0.07642 | ——— | 0.06253 |
| Equiv's. of K transferred | 0.00841 | 0.00839 | ——— | ——— | ——— | 0.00533 | 0.00536 |
| Equiv's. of Na transferred | 0.00547 | 0.00534 | ——— | ——— | ——— | 0.00248 | 0.00251 |
| Wt. of Ag in coulometer | 3.3946 | ——— | ——— | ——— | ——— | ——— | 3.3937 |
| Equiv's. of elec. passed (ave.) | 0.03146 | ——— | ——— | ——— | ——— | ——— | ——— |
| Transference number of K | 0.2673 | 0.2667 | ——— | ——— | ——— | 0.1694 | 0.1704 |
| Transference number of Na | 0.1738 | 0.1697 | ——— | ——— | ——— | 0.1788 | 0.0798 |
| Ratio $T_{Na}/T_K$ | 0.650 | 0.636 | ——— | ——— | ——— | 0.465 | 0.468 |

Kohlrausch at 18° C. (Landolt - Börnstein - Meyerhoff Tabellen) were corrected to 25° C., and the values desired were obtained by careful graphical interpolation.

No explanation can at this time be offered for the nonconcordant results between the anode and cathode portions. As the anode results show by far the more consistent behavior, only they will be used for comparative data. The averages of the anode ratios at each concentration (with the exception that the one obviously low value, 0.636, in Table IV was thrown out) are tabulated below with the corresponding theoretical values.

TABLE VI

Comparison of the Experimental and Theoretical Values of the Ratio $T_{Na} / T_K$

| Concentration (total) | 0.2N | 0.4N | 1.6N |
|---|---|---|---|
| Average anode ratios | 0.673 | 0.663 | 0.643 |
| Theoretical ratios | 0.665 | 0.651 | 0.600 |

E. Discussion of Results

A graphical representation of Table VI (Figure 1) illustrates the comparative tendencies of the two sets of ratios. It will be seen that the experimental ratio is always higher than the theoretical, and that the difference increases roughly as a simple function of the concentration.

These results indicate that more sodium was transferred than theory would call for, and that the "excess" increases with concentration. In other words the sodium gains "transference advantage" with increase of concentration. Such an "advantage" may be due to the

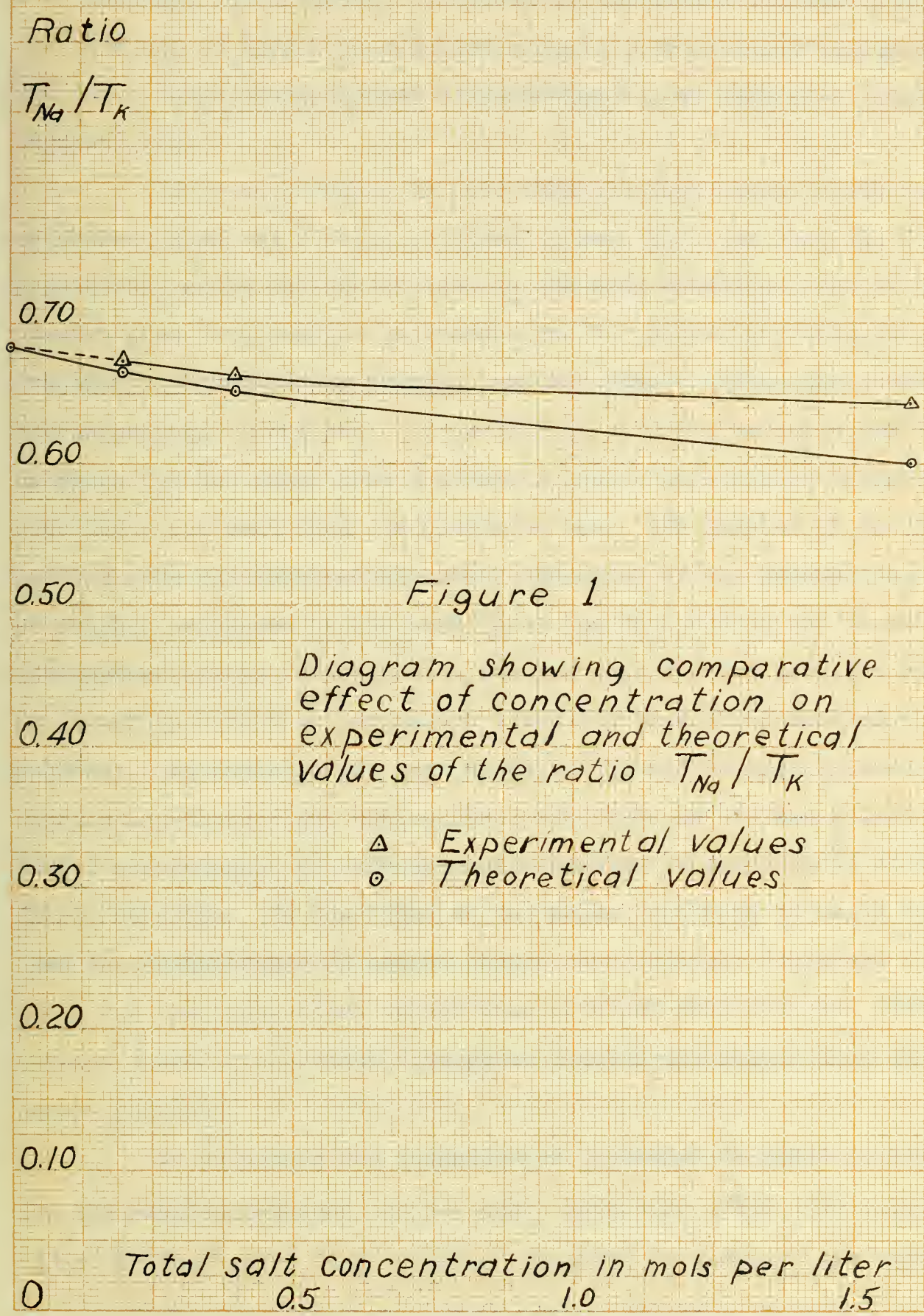


Figure 1

Diagram showing comparative effect of concentration on experimental and theoretical values of the ratio $T_{Na}/T_K$

△ Experimental values
⊙ Theoretical values

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following possible causes,- (1) a direct increase of the simple sodium ion fraction, (2) a relative increase of the sodium ion mobility, (3) the entrance of sodium in superior amounts into positive aggregates, and (4) a "back transference" of potassium in the form of a complex negative ion.

It is interesting to note that the first possibility is in accordance with the results obtained by Ball (1), and that the fourth possibility would indirectly lead to the same condition, for if potassium goes into complex ion formation, the simple potassium ion fraction is subsequently reduced, and the simple sodium ion fraction correspondingly increased. In connection with the second possibility, Washburn (4) has found that the sodium ion is more highly hydrated by over fifty per cent than the potassium ion. And because of the resulting more spacious and unwieldly character of the sodium ion, which is further evidenced by its much lower ion conductance and transference number, it is reasonable to believe that its ion mobility would be slowed up more with increasing viscosity than the potassium ion mobility. Attention might here be called to the assumption made in calculating theoretical values, that the ratio of the equivalent cation conductances at the same concentration is the same as at infinite dilution. In the light of the above reasoning it would follow that the transference of sodium should be relatively decreased even more than the theoretical values thus obtained call for, and that in reality there is a greater divergence between the values than the curves indicate.

If we assume the formation of complexes in order to account for the results obtained, we of course have none other than a qualitative indication of their nature. In order to satisfy the results

obtained both in Ball's work (1) and in this investigation, the complex formation must be of such character to involve an excessive transference of sodium and a diminution of the simple potassium ion fraction, both of which become more pronounced with increase of concentration. Mention was made in the third possible cause given above of the possibility of sodium entering in superior amounts into positive aggregates. This condition might be satisfied by the possible interpolation of Na Cl in the place of the water of hydration of the potassium ion. But as a greater opportunity is afforded for the interpolation of KCl in the more highly hydrated sodium ion, and as the removal of free Na Cl would cut down the sodium ion fraction rather than the potassium ion fraction, this possibility is inconsistent.

The simplest complex formation possible is Na Cl·K Cl, which may be expressed either as K ($NaCl_2$), or Na ($K\ Cl_2$), and which may ionize (as $K_2\ Pt\ Cl_6$) to give either free potassium ions, or free sodium ions. If it should ionize thus,-

$$K\ (Na\ Cl_2) \rightleftharpoons K^+ + Na\ Cl_2^- \quad ,$$

the simple sodium ion fraction would be relatively decreased and a "back transference" of sodium would occur, both of which are contrary to results.

But if it should ionize thus,-

$$Na\ (K\ Cl_2) \rightleftharpoons Na^+ + K\ Cl_2^- \quad ,$$

the sodium ion fraction would be relatively increased, and a "back transference" of potassium would occur, both of which conditions would give an additive tendency to explain the results obtained in both investigations, and which satisfy both the first and fourth possible causes given at the beginning of the discussion.

The fact that the experimental curve extrapolates naturally to the same infinite dilution value as obtained by theory, is an indication of the logical coördination and reliability of the data obtained. This extrapolation can be explained on the basis of complex ion formation, for upon approaching infinite dilution such formations are afforded greater opportunity to dissociate on the basis of the mass law.

It is interesting to note the similar conclusions of S. A. Braley (6) in regard to an investigation of mixed solutions of Na Cl and Sr $Cl_2$ in equilibrium with liquid amalgams, in which it is pointed out that the formation of a complex, Na (Sr $Cl_3$), ionizing thus,-

$$Na\ (Sr\ Cl_3) \rightleftharpoons Na^{+} + Sr\ Cl_3^{-} \quad ,$$

would be in accordance with his results.

## F. SUMMARY

1. This investigation has shown that in equivalent mixtures of Na Cl and K Cl in aqueous solution, a relatively higher amount of sodium is transferred than would be called for on the basis of calculations from conductance of simple solutions in accordance with the isohydric principle.

2. The excess above theory of sodium transferred increases roughly as a simple function of the salt concentration.

3. The results are in harmony with T. R. Ball's (1) results from an investigation of liquid amalgam - mixed solution equilibria, in which he finds that the simple sodium ion fraction increases with increase of total salt concentration.

4. The results may be explained on the basis of complex ion formation, the simplest form of which to give a satisfactory explana-

tion may be expressed thus,-

$$Na\ Cl + K\ Cl \rightleftharpoons Na\ (K\ Cl_2) \rightleftharpoons Na^{+} + K\ Cl_2^{-}$$

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